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AUTHOR(S):

Kumagai, Tetsu

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The Distribution Behavior of Zinc Chloride and Perchlorate Complexes in Acetone-Water Solution by the Cation Exchange Method

Tetsu KUMAGAI*

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The distribution equilibria between zinc chloride complexes and the resin in aqueous acetone solutions have been investigated by cation-exchange method. Formation constants of zinc chloride or perchlorate have been calculated from the distribution coefficients of zinc in aqueous acetone solutions containing 10, 20, 30 and 40 v/v% water respectively by computer. The results are as follows; in 10 v/v% aqueous acetone, $\log \beta_1^{Cl} = 6.05$, $\log \beta_2^{Cl} = 10.45$ and $\log \beta_3^{Cl} = 13.31$ for zinc chloride, $\log \beta_1^{ClO_4} = 1.0$ for zinc perchlorate, and in 20 v/v% aqueous acetone $\log \beta_1^{Cl} = 5.01$, $\log \beta_2^{Cl} = 8.62$, $\log \beta_3^{Cl} = 9.88$, and in 30 v/v% aqueous acetone, $\log \beta_1^{Cl} = 4.42$, $\log \beta_2^{Cl} = 7.06$ and $\log \beta_3^{Cl} = 7.59$, and in 40 v/v% aqueous acetone, $\log \beta_1^{Cl} = 3.95$ and $\log \beta_2^{Cl} = 5.82$ for zinc chloride, respectively.

KEY WORDS: Cation Exchanger/ Acetone-Water/ Zinc Chloride/ Zinc Perchlorate/ Formation Constants/

The investigation on the complex formation and chemical equilibria between metal ion and inorganic anion in nonaqueous solutions are little made compared with those of an aqueous solution, using electrochemical method, solvent extraction and ion-exchange method. In previous papers,⁷⁻⁹⁾ ion-exchange method using the resin for forced-flow chromatography has been employed with remarkable results, and the complex formation constants of zinc halide in aqueous methanol and aqueous or pure ethylene glycol solutions were calculated using this method. Solvent extraction method for nonaqueous solutions, has been studied to gain knowledge on the metal ion equilibrium in nonaqueous systems.¹⁻⁶⁾ But there do not exist so many polar and nonpolar organic solvent pairs immiscible each other, therefore, the use of the solvent extraction method to the chemical equilibria work in nonaqueous system were restricted by the solvent pairs. Zinc chloride and zinc perchlorate complexes in aqueous acetone solutions were studied by the cation-exchange method.

EXPERIMENTAL

The cation exchange resin, Hitachi custom ion-exchange resin 2611, for liquid chromatograph was washed with 1 N hydrochloric acid and distilled water. The H^+ form resin was converted into Na^+ form by 0.2 mol dm⁻³ sodium chloride solution by repeated washing. The resin was stored over phosphorous pentaoxide in a desiccator after removal of excess sodium chloride with distilled water. Zinc-65

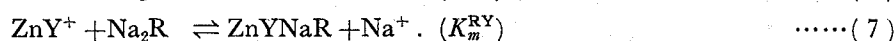
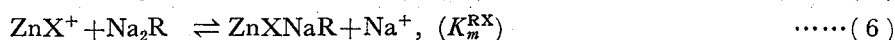
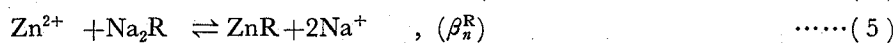
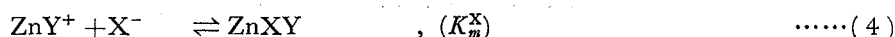
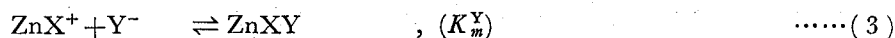
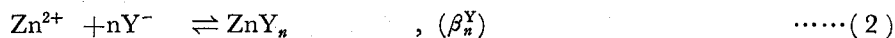
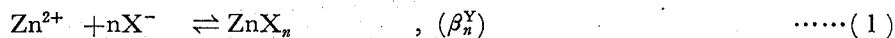
* 熊谷 哲: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

Present Address: Himeji Institute of Technology, Shosha, Himeji, Hyogo 671-22

tracer supplied as the chloride in hydrochloric acid by New England Nuclear, Boston, Mass., U.S.A., was converted into perchlorate by the addition of perchloric acid followed by repeated evaporation. It was dissolved with purified grade acetone. All reagents were guaranteed or more pure grade ones. Dry resin (11 mg–44 mg) and 11 cm³ of an acetone solution containing sodium chloride or sodium perchlorate and zinc perchlorate (1×10^{-6} mol dm⁻³) with radioactivities were added in a 30 ml centrifugal tube equipped with a glass stopper. The solution and the resin were stirred with magnetic stirrer for 3 h in a thermostat at 25°C. After centrifugation, 2 cm³ of supernatant solution was taken in a test tube, and the γ -activities were counted with a well-type scintillation counter, Metro Electronics Model PbW-6. The residual resin was also counted, after the acetone solution was almost removed.

RESULTS AND DISCUSSION

The typical equilibria in the acetone phase are expressed as follows:



Here X⁻ denotes chloride ion, Y⁻ shows perchlorate ion and R stands for the two sulfonic acid groups in the resin.

Total concentration of zinc in the resin phase, (C_{Zn})_R and in the acetone phase, (C_{Zn})_A, are defined or described as follows:

$$(C_{\text{Zn}})_{\text{R}} = m_{\text{ZnR}} + m_{\text{ZnXNaR}} + m_{\text{ZnYNaR}} \quad \dots\dots(8)$$

$$(C_{\text{Zn}})_{\text{A}} = (m_{\text{Zn}} + m_{\text{ZnX}} + m_{\text{ZnX}_2} + m_{\text{ZnX}_3} + m_{\text{ZnY}} + m_{\text{ZnXY}})/\rho. \quad \dots\dots(9)$$

Here ρ is density of the aqueous acetone solution. The distribution coefficient, D , is defined as:

$$D = (C_{\text{Zn}})_{\text{R}}/(C_{\text{Zn}})_{\text{A}}. \quad \dots\dots(10)$$

As the exchange capacity of the resin, about 4.3 meq g⁻¹, was far greater than the amount of zinc perchlorate, the distribution of zinc in the present system was practically independent of the range of 1×10^{-7} – 1×10^{-5} mol dm⁻³ zinc perchlorate as shown in Fig. 1. Then 1×10^{-6} mol dm⁻³ of zinc perchlorate in an acetone solution was used in the subsequent studies. Exchange rate of zinc in an aqueous acetone solution was too fast to measure by ordinary batch method, and the distribution coefficients showed constant values over the stirring in the range 10 min to 48 h. In the present study, the solution was centrifugalized and pipetted after 3 h stirring. The distribution coefficients, the ratio of γ -activities of the resin and the

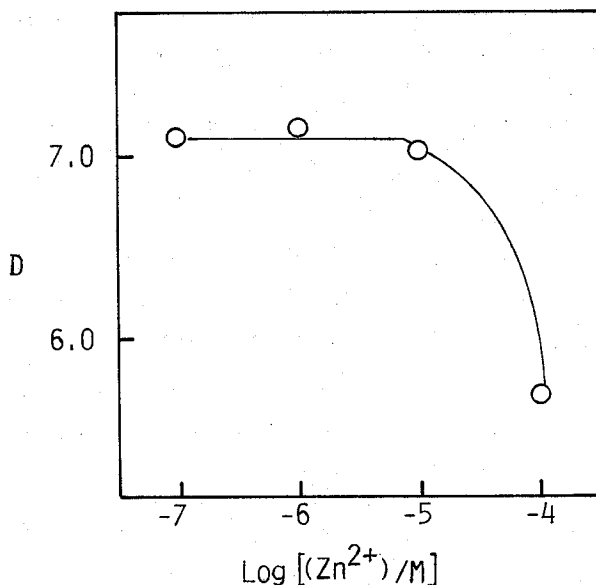


Fig. 1. Influence of initial zinc concentration.
Resin 2.0 g dm⁻¹, NaCl 5 × 10⁻⁴ mol dm⁻³

solution phase, are expressed by using formation constants of Eqs. 1-7 as follows:

$$(C_{Zn})_R = \left(\frac{\beta_2^R}{\gamma_{ZnR} \cdot a_{Na}^2} + \frac{a_X \cdot K_m^{RX} \cdot \beta_1^X}{\gamma_{ZnXNaR} \cdot a_{Na}} + \frac{a_Y \cdot K_m^{RY} \cdot \beta_1^Y}{\gamma_{ZnYNaR} \cdot a_{Na}} \right) \cdot a_{Na_2R} \cdot a_{Zn} \quad \dots\dots (8)'$$

$$(C_{ZnY})_R = (1 + a_X + \beta_1^X a / \gamma_{ZnX} + a_X^2 \cdot \beta_2^X / \gamma_{ZnX_2} + a_X^3 \cdot \beta_3^X / \gamma_{ZnX_3} + a_Y \cdot \beta_1^Y / \gamma_{ZnY} + a_X \cdot a_Y \cdot \beta_1^X \cdot K_m^{XY} / \gamma_{ZnXY}) \cdot a_{Zn} \quad \dots\dots (9)'$$

$$D = m_{Na_2R} \cdot \rho \cdot \left(\frac{\beta_2^R}{\gamma_{Na}^2 \cdot m_{Na}^2} + \frac{\gamma_X \cdot m_X}{\gamma_{Na} \cdot m_{Na}} \cdot K_m^{RX} \cdot \beta_1^X + \frac{\gamma_Y \cdot m_Y}{\gamma_{Na} \cdot m_{Na}} \cdot K_m^{RY} \cdot \beta_1^Y \right) / \left(1 + \sum \gamma_X^n \cdot m_X^n \cdot \beta_n^X / \gamma_{ZnX_n} + \sum \gamma_X^n \cdot m_Y^n \cdot \beta_n^Y / \gamma_{ZnX_n} + \gamma_X \cdot \gamma_Y \cdot m_X \cdot m_Y \cdot \beta_1^X \cdot K_m^{XY} / \gamma_{ZnXY} \right) \quad \dots\dots (10)'$$

Here γ stands for activity coefficient of each ion, γ_{Na_2R} , γ_{ZnR} , γ_{ZnXR} and γ_{ZnYR} can be regarded as 1, and γ_{ZnX_2} , γ_{ZnY_2} , and γ_{ZnXY} are identical. As it is assumed that β_2^R is much greater than β_1^R , β_1^R can be disregarded.

These activity coefficients are calculated from Debye-Huckel's theory. The dielectric constant in aqueous acetone used in Debye-Huckel's treatment are from the data of Albright.¹¹⁾

In the Zn²⁺-X-Y system, m_{Na} , the sum of m_X and m_Y , can keep constant for $I=0.002$ in this study, and in the Zn²⁺-X or Zn²⁺-Y systems, $m_{Na}=m_X$ or $m_{Na}=m_Y$ holds good. Sodium chloride and sodium perchlorate are assumed to dissociate perfectly into ions in the acetone solutions containing not less than 10 v/v% water. It seems that sodium chloride associate partly in 5 v/v% water acetone solution, because sodium chloride was somewhat adsorbed with the resin. Hence, it was difficult to obtain the stability constants of zinc complexes for 5 v/v% aqueous acetone.

In the zinc chloride or perchlorate or chloride-perchlorate systems, Eq. 10' can be reduced to

$$D^* = \frac{(P_{(1)} + P_{(2)} \cdot m_X + P_{(3)} \cdot m_Y) \cdot m_{Na_2R}}{1 + P_{(4)} \cdot m_X + P_{(5)} \cdot m_X^2 + P_{(6)} \cdot m_X^3 + P_{(7)} \cdot m_Y + P_{(8)} \cdot m_X \cdot m_Y} \quad \dots\dots(11)$$

Here $D^* = D \cdot \gamma_{Na}^2 \cdot m_{Na}^2 / \rho$, $(P)_{(1)} = \beta_2^R$

$$P_{(2)} = \beta_1^X \cdot K_m^{RX} \cdot \gamma_X \cdot \gamma_{Na} \cdot m_X \cdot m_{Na}, \quad P_{(3)} = \beta_1^Y \cdot K_m^{RY} \cdot \gamma_{Na} \cdot \gamma_Y \cdot m_{Na} \cdot m_Y$$

$$P_{(4)} = \gamma_X \cdot \beta_1^X / \gamma_{ZnX}, \quad P_{(5)} = \gamma_X^2 \cdot \beta_2^X, \quad P_{(6)} = \gamma_X^3 \cdot \beta_3^X / \gamma_{ZnX},$$

$$P_{(7)} = \gamma_Y \cdot \beta_1^Y / \gamma_{ZnY}, \quad P_{(8)} = \gamma_X \cdot \gamma_Y \cdot m_X \cdot m_Y \cdot \beta_1^X \cdot K_m^Y.$$

In the zinc chloride system, the term of Y are set to zero, that is $m_Y = 0$, $\beta_Y = 0$, and $\gamma_Y = 0$. In the zinc perchlorate system the terms relating to X are neglected. In the zinc chloride perchlorate system, $\beta_n^X \gg \beta_n^Y$ is well hold good, and consequently the terms of β_n^Y can be neglect under calculation of Eq. 11. Parameters, $P_{(i)}$, were calculated by computer used least-squares method and the values obtained by this procedure were confirmed by curve fitting method, using computer graphics. Figures 2-5 show the dependence of $\log D^*$ on the chloride activity calculated using Eq. 11 and by Debye-Huckel's treatment in the aqueous acetone containing from 10 v/v% to 40 v/v% water. These figures show that the decrease of $\log D^*$ is much greater in lower chloride activity range than in higher chloride activity range, and these activity range are shifted to higher level with the increase of water in acetone solution. The distribution of zinc at constant ionic strength is shown in Fig. 6.

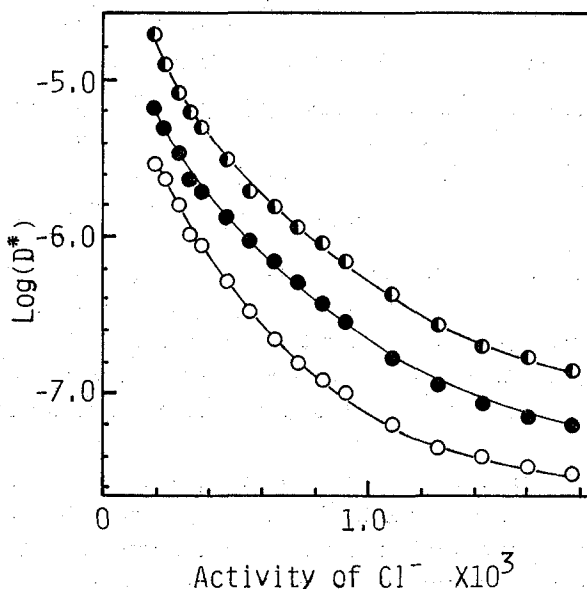


Fig. 2. Distribution coefficients of zinc in 10% aqueous acetone solution.

Resin amounts; \bigcirc 1 g dm⁻³, \bullet 2 g dm⁻³,
 \bullet 4 g dm⁻³.

Zinc Chloride and Perchlorate in Aqueous Acetone

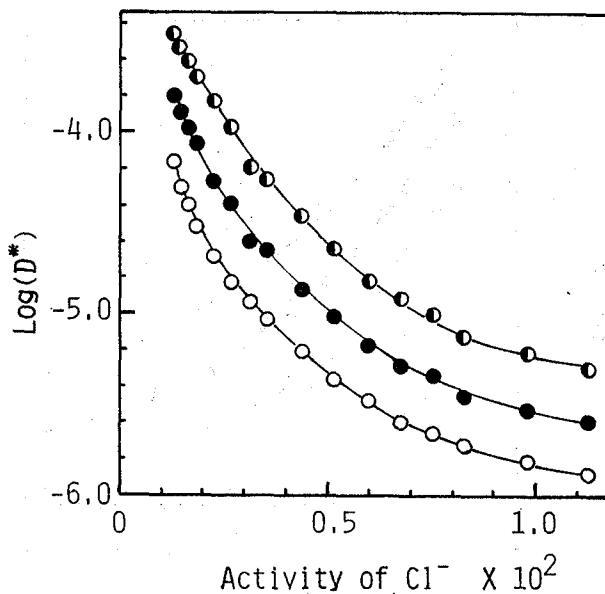


Fig. 3. Distribution coefficients of zinc in 20% aqueous acetone solution.

Resin amounts; $\circ 1 \text{ g dm}^{-3}$, $\bullet 2 \text{ g dm}^{-3}$,
 $\bullet 4 \text{ g dm}^{-3}$.

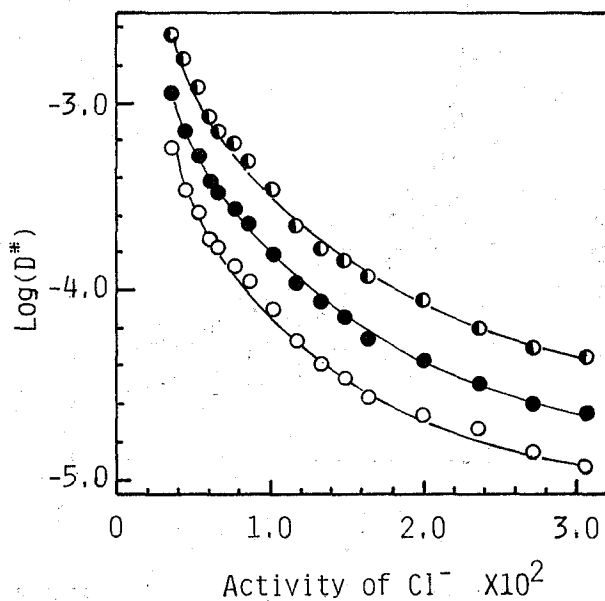


Fig. 4. Distribution coefficients of zinc in 30% aqueous acetone solution.

Resin amounts; $\circ 1 \text{ g dm}^{-3}$, $\bullet 2 \text{ g dm}^{-3}$,
 $\bullet 4 \text{ g dm}^{-3}$.

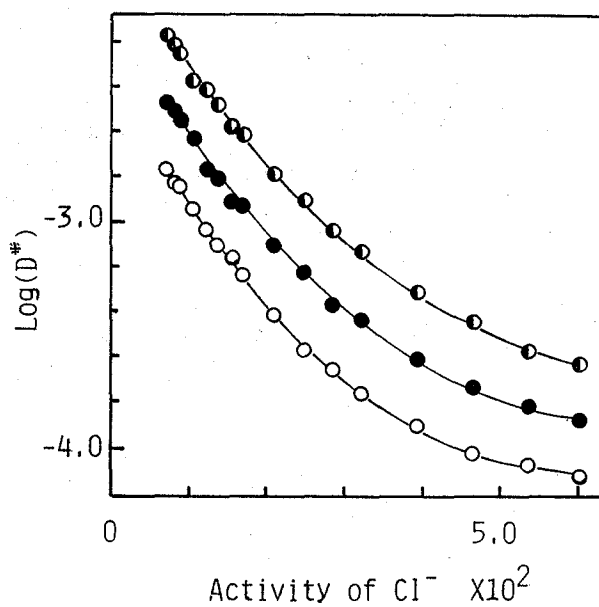


Fig. 5. Distribution coefficients of zinc in 40% aqueous acetone solution.

Resin amounts; \circ 1 g dm^{-3} , \bullet 2 g dm^{-3} ,
 \bullet 4 g dm^{-3} .

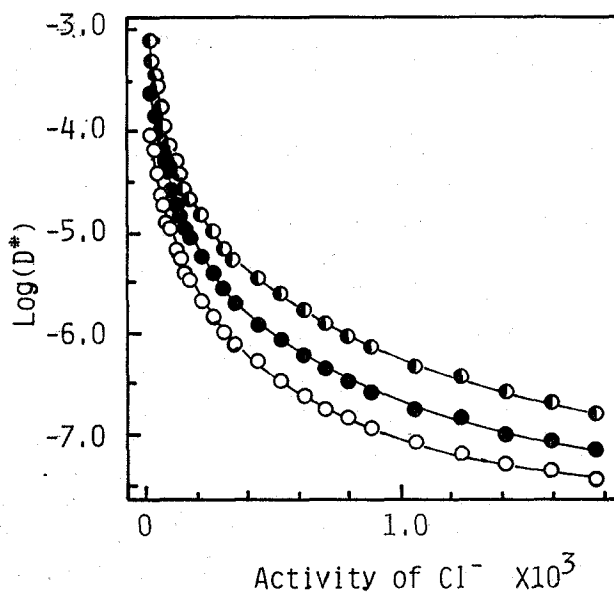


Fig. 6. Distribution coefficients of zinc in 10% aqueous acetone solution in NaCl-NaClO_4 system, at constant ionic strength.

I ; 0.002,
 Resin amounts; \circ 1 g dm^{-3} , \bullet 2 g dm^{-3} ,
 \bullet 4 g dm^{-3} .

As formation constants of zinc perchlorate, $\beta_n^{\text{ClO}_4}$, is much smaller than that of zinc chloride, β_n^{Cl} , the distribution behavior of zinc in Fig. 2 is nearly identical with that in Fig. 6. This result was confirmed by the distribution of zinc in sodium perchlorate solution as is shown in Fig. 7. The distribution of zinc is gradually decrease in the perchlorate activity range investigated, and the value of β_n^{Cl} is increased about orders of magnitude over the value than that of $\beta_1^{\text{ClO}_4}$. The stability constants obtained from the treatment of distribution coefficients by using the program described above are listed in Table I. There are little difference between the β_n in the sodium chloride system and β_n in the sodium chloride-perchlorate system without the variation of ionic strength. Figure 8 indicates the dependence of stability constants, β_2 , on the molarity of water in aqueous acetone solution. Logarithm of β_2 is concavely decreased from pure acetone to pure water with increase of water molarity.¹⁰⁾

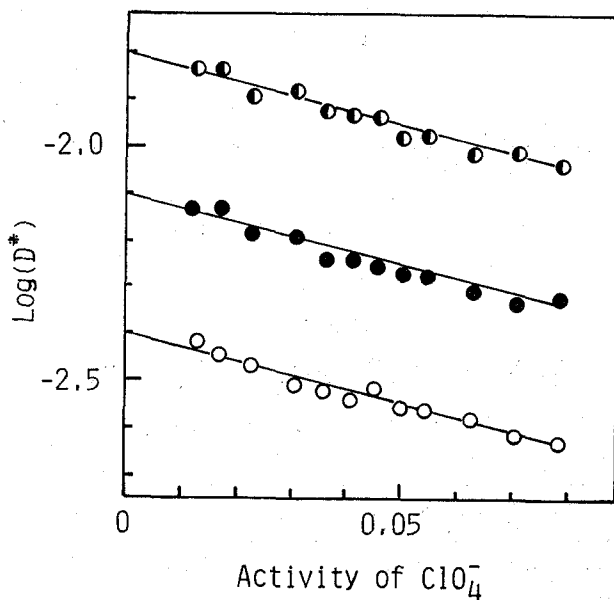


Fig. 7. Distribution coefficients of zinc in 10% aqueous acetone solution in zinc perchlorate system.

Resin amounts; ○ 1 g dm⁻³, ● 2 g dm⁻³,
◐ 4 g dm⁻³.

Table I Stability constants of zinc chloride and zinc perchlorate.

		$\log \beta_1^X$	$\log \beta_2^X$	$\log \beta_3^X$
X=Cl,	10% water	6.02 ± 0.05	10.45 ± 0.05	13.31 ± 0.08
X=Cl,	20% water	5.01 ± 0.05	8.62 ± 0.05	9.88 ± 0.08
X=Cl,	30% water	4.42 ± 0.05	7.06 ± 0.05	7.59 ± 0.08
X=Cl,	40% water	3.95 ± 0.04	5.82 ± 0.05	—
X=ClO ₄ ,	10% water	1.0 ± 0.04	—	—
X=Cl,	10% water (I=0.002)	6.07 ± 0.05	10.49 ± 0.05	13.29 ± 0.08

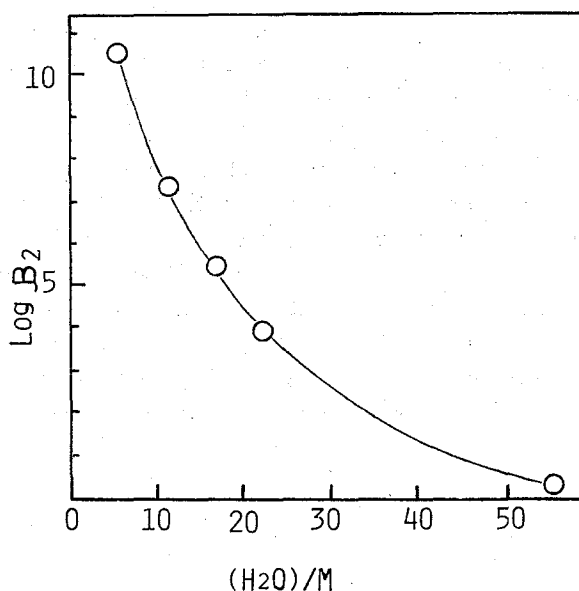


Fig. 8. Stability constants of zinc chloride on various water molarity.

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